

RELATIVE AGES OF MASKELYNITE AND CARBONATE IN ALH84001 AND IMPLICATIONS FOR EARLY HYDROTHERMAL ACTIVITY ON MARS -- David A. Kring, Timothy D. Swindle, James D. Gleason, and Jennifer A. Grier, Lunar and Planetary Laboratory, University of Arizona, 1629 E. University Blvd., Tucson, AZ 85721.

ALH84001 is the first SNC-related orthopyroxenite [1] and apparently the first sample from the ancient cratered highlands of Mars. Isotopic analyses indicate it crystallized ~4.5 Ga [2,3], forming some of the original crust of Mars only a few hundred million years after planetary differentiation. Subsequently, the cumulate was repeatedly shock-metamorphosed and invaded by CO₂-charged hydrothermal fluids which produced secondary carbonate. One of the shock-metamorphic events appears to have occurred ~4.0 Ga [e.g., 4], although the timing of other impact events and the precipitation of secondary carbonate is uncertain [cf., 5–7]. To further constrain the timing of these events, we have examined the textural relationship between the cumulate minerals and features produced by secondary metamorphic and hydrothermal processes.

The original cumulate fabric of the rock (split, 140) is crosscut with cataclastic zones of anhedral to subhedral orthopyroxene, chromite, and feldspathic glass [8]. Carbonate occurs in these cataclastic zones and in fractures between and within surviving orthopyroxene. It is clear that the carbonate precipitated after the impact event that produced the cataclastic zones of material, because the carbonate is not dis-aggregated. Rather, its crystal fabric crosscuts the disorganized structure of the cataclastic zones and fractured orthopyroxene.

Where igneous textures are best preserved, the feldspathic glass occurs interstitially between euhedral to subhedral orthopyroxene grains. The morphology and stoichiometry of the glass indicates it is maskelynite, a diaplectic glass produced from plagioclase (Ab₆₀An₃₆Or₄) by shock pressures >29 GPa [9]. Carbonate is intimately associated with the feldspathic glass. They occur together in the cataclastic zones, occupying the same morphological niches, and elsewhere patches of carbonate invade larger grains of maskelynite. Like Treiman [10], we believe these types of textures indicate the carbonate was produced in a dissolution-precipitation reaction. Unlike Treiman [10], however, we think the carbonate grew at the expense of maskelynite rather than plagioclase. As several investigators have noted [e.g., 1,10,11], the carbonate has a radial crystalline texture which produces spherical or semi-spherical globules. This morphology is consistent with the replacement of

a glassy phase [e.g., 12–15] or growth into liquid or vapor. In contrast, when carbonate replaces plagioclase, it usually attacks boundaries between crystal twins, grain boundaries, and cracks. This produces linear traces or skeletal frameworks of carbonate rather than semi-spherical globules of radiating carbonate. Consequently, the texture of the carbonate suggests it replaced maskelynite and is thus younger than maskelynite. Carbonate replacement of maskelynite has previously been documented in shock-metamorphosed rocks associated with the Clearwater West impact crater on Earth [16,17].

The duration of hydrothermal activity needed to produce the carbonate can be estimated by considering the dissolution rate of maskelynite. The dissolution rate is dependent on the pH of the hydrothermal fluid. Previous assessment of the assemblage of carbonate, ZnS, Fe-sulfides, and Fe-sulfates in ALH84001 suggests the dissolution occurred in a system where pH>7 [18]. In a mildly to strongly alkaline system, experimental results [19] indicate that plagioclase with the ALH84001 composition of Ab₆₀An₃₆Or₄ would dissolve at a rate of 1.9×10^{-10} μm/s (pH=7, T=22°C) to 1.4×10^{-12} μm/s (pH=12, T=22°C). At these rates, 50 μm of plagioclase (equivalent to the approximate radius of carbonate globules) could be dissolved in 8,300 yrs to 1.1 million yrs. Since we believe carbonate replaced maskelynite rather than plagioclase, the applicable dissolution rate may have been a little faster, but not as fast as the dissolution rate of a completely disordered glass. If hydrothermal fluids were hotter than ~22°C, then the dissolution rate would have been even faster. For example, experimental dissolution of tektite glass at 90°C [20] and an-desitic glass at 300°C [21] suggests time scales as short as a few years are possible. According to Wentworth and Gooding [18], the carbonate may have been produced at temperatures of ~100–300°C, in which case the hydrothermal system that affected ALH84001 may have been very short lived. If the temperatures were even higher, like those (>650°C) proposed by Harvey and McSween [11], then the dissolution-precipitation reaction would have occurred very quickly.

If the temperatures of the hydrothermal system were >650°C, then the ⁴⁰Ar-³⁹Ar systematics in the

maskelynite would have been reset while the carbonate precipitated [7]. In this case, the age of the carbonate would correspond to the last degassing age of the maskelynite, ~4.0 Ga [4,5,7]. On the other hand, if the temperature of the hydrothermal system was <300 °C, then the ^{40}Ar - ^{39}Ar systematics in the maskelynite may have only been disturbed and the carbonate could have an age significantly less than 4.0 Ga. Previous attempts to determine the timing of the carbonate precipitation have suggested younger ages, with estimates ranging from 3.6 Ga [5] to 1.39 Ga [6]. The youngest age is based on a poorly constrained two-point Rb-Sr “isochron” produced during a leaching experiment. The older age is based on a preliminary laser ^{40}Ar - ^{39}Ar analysis which the authors now conclude was misleading [7]. They feel that the Ca/K ratio in that analysis is lower than they expect in carbonate, and conclude that their sample must have included some phase richer in K. We tried to measure the abundances of K in maskelynite and carbonate with an electron microprobe to see if we could extract the age of the carbonate based on the Ca/K ratios of this and other ^{40}Ar - ^{39}Ar analyses. We determined that maskelynite contains ~6,000 ppm K and has a Ca/K ratio of ~8. The Mg,Fe-carbonate and Mg-carbonate have <80 ppm K and Ca/K ratios >380 and >310, respectively. Most of the carbonate-bearing material analyzed by Turner *et al.* [7] have much larger K abundances than we measured in carbonate and consequently we confirm their conclusion that they were probably not dating the carbonate. However, we also note that they have three samples with K<120 ppm, approaching the values expected of carbonate, and that these three samples also have systematically lower apparent ages, suggesting the carbonate is younger than the ~4.0 Ga degassing age of maskelynite. We conclude that dating of carbonate using the ^{40}Ar - ^{39}Ar technique may be feasible, but probably requires larger and/or purer samples.

Finally, we note that if carbonate was produced at the expense of maskelynite in an atom-by-atom dissolution-precipitation reaction, then it is not likely

to have involved microbial life [*cf.*, 22]. The radiating globular textures of the carbonate are consistent with the nucleation and growth kinetics of reactions involving glassy materials like maskelynite. We also point out that Ca-carbonate, with radiating crystal fibers in globular forms with about the same dimensions (50 μm diameter) as seen in ALH84001, have been described in CI chondrites [23]. In the case of the CI carbonate, it seems clear that the textures were produced by simple aqueous activity; one cannot, therefore, appeal exclusively to microbial intervention for the textures seen in ALH84001 unless one also argues that CI-chondrite parent bodies harbored life.

References: [1] D.W. Mittlefehldt (1994) *Meteoritics* 29, 214–221. [2] E. Jagoutz *et al.* (1994) *Meteoritics* 29, 478–479. [3] L.E. Nyquist *et al.* (1995) *LPS XXVI*, 1065–1066. [4] R.D. Ash *et al.* (1996) *Nature* 380, 57–59. [5] S.F. Knott *et al.* (1995) *LPS XXVI*, 765–766. [6] M. Wadhwa and G.W. Lugmair (1996) *Meteoritics Planet. Sci.* 31, A145. [7] G. Turner *et al.* (1997) *GCA*, in press. [8] J.D. Gleason *et al.* (1997) *GCA*, submitted. [9] D. Stöffler *et al.* (1986) *GCA* 50, 889–903. [10] A. Treiman (1995) *Meteoritics* 30, 294–302. [11] R.P. Harvey and H.Y. McSween Jr. (1996) *Nature* 383, 49–51. [12] H.D. Keith and F.J. Padden Jr. (1963) *J. Appl. Phys.* 34, 2409–2421. [13] H.D. Keith and F.J. Padden Jr. (1963) *J. Appl. Phys.* 35, 1270–1285. [14] H.D. Keith and F.J. Padden Jr. (1963) *J. Appl. Phys.* 35, 1286–1296. [15] G. Lofgren (1971) *JGR* 76, 5635–5648. [16] M.R. Dence (1965) *Annals NY Acad. Sci.* 123, 941–969. [17] T.E. Bunch *et al.* (1967) *Am. Min.* 52, 244–253. [18] S.J. Wentworth and J.L. Gooding (1995) *LPS XXVI*, 1489–1490. [19] S.A. Welch and W.J. Ullman (1996) *GCA* 60, 2939–2948. [20] P.H. LaMarche *et al.* (1984) *J. Non-Crystal. Solids* 67, 361–369. [21] R.N. Guillemette *et al.* (1980) *Proc. Internat. Symp. Rock-Water Interaction*, 3rd, p. 168–169. [22] D.S. McKay *et al.* (1996) *Science* 273, 924–930. [23] K. Fredricksson and J.F. Kerridge (1988) *Meteoritics* 23, 35–44.